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**Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation and Recycle of Sodium Hydroxide and Sodium Nitrate**

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FY 2001 Annual Report to be submitted to the Environmental Management Science Program and to be posted on the internet.

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## **Project 65339 FY 2001 Annual Report**

### *Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation and Recycle of Sodium Hydroxide and Sodium Nitrate*

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Number of graduate students: 3 (UNT)

Number of postdocs: 9 (2 at ORNL and 7 at UNT)

## Research Objective

Disposal of high-level nuclear waste is horrendously expensive, in large part because the actual radioactive matter in the tanks has been diluted over 1000-fold by ordinary inorganic chemicals. Treatment processes themselves can exacerbate the problem by adding further volume to the waste. Waste retrieval and sludge washing, for example, will require copious amounts of sodium hydroxide. If the needed sodium hydroxide could be separated from the waste and recycled, however, the addition of fresh sodium hydroxide could be avoided, ultimately reducing the final waste volume and associated disposal costs.

The major objective of this research is to explore new liquid-liquid extraction approaches to the selective separation of sodium hydroxide from alkaline high-level wastes stored in underground tanks at the Hanford and Savannah River sites. Consideration is also given to separating potassium and abundant anions, including nitrate, nitrite, aluminate, and carbonate. Salts of these ions represent possible additional value for recycle, alternative disposal, or even use as commodity chemicals.

A comprehensive approach toward understanding the extractive chemistry of these salts is envisioned, involving systems of varying complexity, from use of simple solvents to new bifunctional host molecules for ion-pair recognition. These extractants will ideally require no adjustment of the waste composition and will release the extracted salt into water, thereby consuming no additional chemicals and producing no additional waste volume. The overall goal of this research is to provide a scientific foundation upon which the feasibility of new liquid-liquid extraction chemistry applicable to the bulk reduction of the volume of tank waste can be evaluated.

## Research Progress and Implications

This report summarizes work performed during the final 15 months of a three-year project. Experiments have focused on identifying candidate extraction systems possessing appreciable loading, effective stripping with water, and adequate selectivity for hydroxide. Of eight possible fundamental approaches to developing such extractants, three have proven most promising and have received focused attention. All three approaches employ a cation-exchange principle in which a very weakly acidic reagent exchanges a proton for sodium ion at elevated pH values characteristic of alkaline tank waste. Contact of the solvent phase with water then regenerates the neutral alcohol by hydrolysis, releasing sodium hydroxide into the water. Based on this principle, the first type of system entails use of alkylated phenols or fluorinated alcohols as cation exchangers for sodium. Since hydroxide ion is not actually extracted, this type of system has been designated "pseudo hydroxide extraction." When the cation exchangers are combined with macrocyclic sodium ion receptors, the second type of system, designated "synergized pseudo hydroxide extraction" is obtained. A third type of system employs ditopic macrocyclic sodium ion receptors containing ionizable groups for cation exchange of sodium.

As an example of "pseudo hydroxide extraction," the fluorinated alcohol 1H,1H,9H-hexadecafluorononanol (HDFN) in 1-octanol has sufficient acidity to be converted to its sodium salt when contacted with highly alkaline aqueous solutions. Using 1-octanol as a diluent, a series of fluorinated alcohols and selected lipophilic phenols were shown in the first two years of the project to exhibit selective extraction of sodium. Simple aqueous phases, such as sodium nitrate and sodium hydroxide mixtures, as well as complex waste simulants were successfully treated.

Quantitative recovery of sodium hydroxide from the loaded solvents by stripping with water was demonstrated, and it was shown that sufficiently lipophilic extractants could be cycled several times without loss of performance. Selectivity for hydroxide over nitrate transfer exceeds 20:1. Efforts in the past year have addressed several issues pertaining to solvent capacity. It has been found that good loading of the solvent exceeding 1 M sodium can be achieved, but high solvent viscosity or even gelation occurs at 25 °C. This may be overcome by performing extraction and stripping at 60 °C, and isotherms have been obtained for several candidate extractants. It was shown that greater than 90% of the free hydroxide in a simple tank-waste simulant (alkaline nitrate solution containing aluminate) may be recovered. At least two extractants appear to be viable for process use in terms of efficacy and cost. Caustic recycle applications include recycle of sodium hydroxide at several DOE sites as well as in certain industrial processes. A patent application has been filed and is near issuance as a first step toward attracting users and ultimately transferring the technology. A spin-off proposal to the EM-50 Efficient Separations and Processing Crosscutting Program was funded in FY01 and FY02 to adapt this technology to a Hanford application.

As a first demonstration of “synergized pseudo hydroxide extraction,” exciting synergistic effects in sodium hydroxide separation have been discovered by combining fluorinated alcohols with macrocyclic extractants. Prof. Alan Marchand and his group at the University of North Texas are carrying out synthesis of novel crown ethers and podands. The UNT group has devised workable synthetic methodology to produce a series of novel cage-annulated oxa- and aza-crown ethers (a) that possess varying cavity sizes and shapes and (b) that differ in the number and nature of the donor atoms contained in the macrocyclic system. A crystal structure of one of the aza macrocycles, as an HCl salt, has been determined, providing valuable information on the macrocycle’s preferred conformation. By appropriate variation of macrocycle structure, the strength and selectivity of extraction of alkali metal cations may be controlled, as shown in standard picrate extraction surveys. Although the macrocycles used alone tend to favor the extraction of sodium salts of large anions, sodium extraction from hydroxide solutions jumps sharply when the macrocycles are added to active fluorinated alcohols. Large synergistic effects have been recorded, sufficient to make hydroxide separation competitive with the more abundant nitrate. These successful prototype systems have provided valuable information that is guiding continuing efforts to design more effective host species. One such direction entails ditopic pseudo hydroxide extractants, and a first example was successfully synthesized and delivered to ORNL.

## **Planned Activities**

During the final two months of the project, study of the extraction behavior of the ditopic receptor mentioned above will be initiated. The primary goal will be to demonstrate that pseudo hydroxide extraction is operating and to initiate evaluation of whether the ditopic receptor offers advantages over the simpler synergized pseudo hydroxide extraction.

In the renewal 3-year period, a collaborative project involving Oak Ridge National Laboratory, Pacific Northwest National Laboratory (G. J. Lumetta), and the University of North Texas (Prof. A. P. Marchand) will be undertaken to explore new approaches to the separation of sodium hydroxide, sodium nitrate, and other sodium salts from high-level alkaline tank waste. The principal potential benefit of this research will be a major reduction in the volume of the high-activity waste stream, obviating the building of expensive new waste tanks and reducing the costs of vitrification. Principles of ion recognition will be researched toward discovery of liquid-

liquid extraction systems that selectively separate sodium hydroxide and nitrate from waste-like matrices. Successful approaches to sodium hydroxide separation that were discovered in the prior three years will be enhanced by further efforts to understand the underlying properties of the controlling equilibria. This work will employ the novel concept of pseudo hydroxide extraction by fluorinated alcohols and phenols that function by cation exchange at elevated pH values. Crown ethers designed for sodium binding will be examined as possible synergists, and new ionizable lariat ethers will be synthesized as a new class of pseudo hydroxide extractants (UNT). A new thrust will be initiated to specifically target sodium nitrate. Applicable principles to be understood include solvation effects that promote efficient sodium nitrate extraction and appropriate crown ether design for efficient sodium binding and rejection of cesium. A proposed approach to the combined removal of sodium salts will be examined. Studies with real tank waste at PNNL will provide feedback toward solvent designs that have desirable properties.

### **Information Access**

A complete list of publications, patent application, and presentations for this project is also available as optional additional information associated with this annual report. See also www home page of the ORNL Chemical Separations Group: <http://www.ornl.gov/csg>.

## PUBLICATION LIST

### **Ion Recognition Approach to Volume Reduction of Alkaline Tank Waste by Separation and Recycle of Sodium Hydroxide and Sodium Nitrate**

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#### Patent Status

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